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## High temperature mechanical behavior of porous cordierite-based ceramic materials evaluated using 3-point bending

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### Abstract

Cordierite-based ceramics are an important segment of the present ceramic industry. In the last years, cordierite-based porous ceramics have received great attention as light structural materials, thermal insulating and catalyst supports, among others. For these applications, a combination of high porosity and low weight of the component are required, together with mechanical stability even at high temperatures which might prevail in use. The combination of these requirements is a challenge due to the compromise existing among them. In this work, materials prepared from two precursor mixes of cordierite based on kaolin, talc and alumina by thermal consolidation (80 °C, 4 h) of stable aqueous suspensions mix-starch were evaluated. Two different native starches, potato and corn, were employed. The starch gel, which acted as binder in the green body, generated the pores when it was eliminated during a further thermal treatment (650 °C, 2 h). The transformation of the raw materials in cordierite was carried out by reaction-sintering at 1330 °C, 4 h. Cylindrical bars of 35-50 mm in length and 3.5-4.0 mm in diameter were prepared using this method, and then, they were mechanically tested from room temperature to 1100 °C using 3-point bending. A servohydraulic testing machine INSTRON 8501 and a SiC fixture (span: 30 mm) were used for the mechanical testing. The tests were performed in displacement control with a constant rate of 0.1 mm/min. The difference observed in the behavior and the mechanical parameters (Young modulus and mechanical strength) of final materials were related with the characteristics of raw materials and their composition, texture and microstructure, especially porosity and the presence of glassy phase.

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## 1. Introduction

Porous cordierite materials ( $5\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{MgO}$ ) are candidates to be used as thermal insulators due to their low thermal expansion coefficient ( $3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) and low thermal conductivity (1-2 W/mK) (Alves et al. (1998)). In recent years, novel processing routes have been proposed with the aim of developing these materials with chemical compositions and porous microstructures adequate to this application (Studart et al. (2006), Sigmund et al. (2000)). In particular, the forming methods by direct consolidation of ceramic suspensions in which a gelling agent acts as a consolidator/binder of the ceramic particles and a pore former at high temperature, are promising routes for developing of porous ceramics with controlled microstructures. Thus, the ‘starch consolidation casting’, is a relatively new non-contaminating technique of low-cost, in which the insolubility of starch granules in water at temperatures less than 50 °C, and the ability to form gels in aqueous medium at temperatures between 55-85 °C (Lyckfeldt and Ferreira (1998), Barea et al. (2005), Talou and Camerucci (2010), Gregorová and Pabst (2011)) are utilized. After calcination and sintering treatments, a material with porosity associated mainly with open pores, whose characteristics are related to amount, size and morphology of swelled starch granules, is obtained.

However, the pores incorporated into the material in order to favor its capacity to insulate heat, also impoverish its mechanical properties. Moreover, in its use as thermal insulator as well as in many others applications, ceramic materials are subjected to high temperatures and thermal gradients which originate residual stresses and degrade its mechanical resistance. However, the mechanical evaluation of porous materials at high temperature in order to determine their performance in conditions close to those in service is uncommon.

In this paper, the mechanical behavior of porous cordierite-based materials evaluated using 3-point bending is studied. Cordierite materials were formed by: (1) starch consolidation casting using aqueous suspensions of two precursor mixtures, one of them composed by kaolin, talc and alumina powders, and the other, a commercial powder, and two commercial starches (corn and potato), (2) calcination, and (3) reaction-sintering. The mechanical response of developed materials was evaluated as a function of temperature up to 1100 °C, in relation to microstructural and textural characteristics, in particular, the presence of glassy phase and porosity.

## 2. Materials and methods

### 1.1. Raw materials

Two cordierite precursor mixtures, one of them formulated with commercial powders of talc (Talc EC75, Australia), alumina (CT3000 SG, Almatiss, Germany) and kaolin (CZ-Sedlec Ia, Czech Republic), and the other one a commercial mixture (Czech Republic) supplied in the form of granulated powder, were employed. Moreover, commercial native starches of potato (Solamyl de Natura a.s., Czech Republic) and corn (Gustin from Dr. Oetker, Czech Republic) were used. The characteristics of ceramic powders (kaolin, talc and alumina) as well as those of potato and corn starches were reported in previous works of the authors (Lambertini et al. (2013)).

The X-ray fluorescence (XRF) analysis of the raw materials used to obtain one of the cordierite precursor mixture, denoted as MCZ, indicated that the kaolin has a  $\text{Al}_2\text{O}_3/\text{SiO}_2$  weight ratio close to 0.8, which corresponds to the stoichiometric proportion of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), the main clay component of this mineral, with amounts of  $\text{Fe}_2\text{O}_3$ , CaO, MgO and  $\text{Na}_2\text{O} < 1.9 \text{ wt\%}$  and  $\sim 0.9 \text{ wt\%}$  of  $\text{K}_2\text{O}$ . Regarding the other constituents of the precursor mixture, also the talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) exhibits a  $\text{SiO}_2/\text{MgO}$  weight ratio ( $64.4/33.1=1.9$ ) close to the stoichiometric composition, with contents of  $\text{Fe}_2\text{O}_3$  (0.9 wt%) and CaO (0.4 wt%) as impurities. The alumina powder ( $\text{Al}_2\text{O}_3$ ) showed a high purity (99.85 wt%), with an alkaline and alkaline earth impurity levels lower than 0.2 wt% and a very small amount of silica and iron oxides (0.05 wt%).

The precursor mixture MCZ has 37 wt% of kaolin, 41 wt% of talc and 22 wt% of alumina. It was formulated based on its compositions in oxides and bears some resemblance to stoichiometric cordierite ( $\text{SiO}_2 = 51.4 \text{ wt\%}$ ,  $\text{Al}_2\text{O}_3 = 34.8 \text{ wt\%}$  and  $\text{MgO} = 13.8 \text{ wt\%}$ ). However, it has a lower silica content (46.6 wt%) and a higher alumina content (38.1 wt%) than the stoichiometric composition, whereas the magnesia content is very similar (13.6 wt%).

Concerning the commercial precursor mixture, labeled as ‘Premix’, it was characterized by X-ray diffraction (XRD) using a X’Pert PRO, PANalytical equipment ( $\text{CuK}_\alpha$  radiation, 40 kV, 40 mA and a rate of  $1^\circ/2\theta/\text{min}$ ). Alumina as corundum ( $\alpha\text{-Al}_2\text{O}_3$ ), quartz ( $\text{SiO}_2$ ) and kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) were identified as main phases, along

with talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) and halloysite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). The granulated powder presented a wide particle size distribution (Analysette 22 NanoTec, Fritsch) composed by three overlapped fractions with sizes between 0.5 and 20  $\mu\text{m}$ . An additional fraction between 20 and 80  $\mu\text{m}$  of particles size was associated with the presence of agglomerates of the smallest particles.

Potato and corn starches had real densities (measured by He-pycnometry) of 1.47  $\text{g}/\text{cm}^3$  and 1.49  $\text{g}/\text{cm}^3$ , respectively. Both starches presented bimodal particle size distributions, with median volume diameter ( $D_{50}$ ) of 45  $\mu\text{m}$  for potato starch and 15  $\mu\text{m}$  for corn starch, and low volume percentage of small particles, which were associated with impurities or broken granules. The humidity percentages (determined by TGA) were 14.4 % for potato and 11.5 % for corn starch, both values being in the range of those usually reported for each type of starch (Srichuwong et al. (2005), Mao et al. (2008)). By SEM observation was determined that potato starch exhibited the largest granules, with smooth surfaces and oval or spherical forms, while the granules of corn starch showed a polyhedral morphology.

## 2.2. Preparation and characterization of porous cordierite-based materials

Aqueous ceramic (MCZ or Premix)-starch (potato or corn) suspensions with solid contents of 60 wt% were prepared by: (a) mixing (impeller mixer) ceramic powders in distilled water (70.4 vol%) with 1 wt% of Dolapix CE-64 (Zschimmer & Schwarz, Germany) and 0.5 wt% of sodium naphthalenesulfonate (Nutrimer, Argentina), both amounts with respect to the ceramic solid content, added in a sequential manner (the kaolin suspension first, with a pause of 24 h, then the talc and finally the alumina); (b) homogenizing in a ball mill for 4 h; (c) degassing for 20 min, and after homogenizing the inorganic solids, (d) 25 wt% of starch and extra water in order to fit the total solid content to the solid concentration (60 wt%) were added and homogenized into the ceramic suspension by mixing at a low rate for 1–2 min to avoid the rupture of starch granules, and thus, in consequence, to avoid the possible occurrence of an incipient gelatinization process at room temperature. Subsequently, the ceramic-starch suspension was degassed in vacuum for 20 min. The volume fraction of starch related to suspension volume was calculated in 15 vol% considering a pycnometric density of  $(2.40 \pm 0.05) \text{ g}/\text{cm}^3$  for the precursor mixture with starch (determined by He-pycnometry).

Cylindrical bars with final dimensions of 35–50 mm in height and 3.5–4.0 mm in diameter were formed by thermal consolidation of aqueous suspensions of the cordierite precursor mixtures with starch. Experimental conditions (temperature and dwell time) used for the consolidation of suspensions were established on the basis of results previously reported by the authors (Sandoval et al. (2009), Sandoval et al. (2010)) and other data reported in the literature (Alves et al. (1998)). The suspensions were poured into cylindrical bronze molds, which were heated in an electric stove with forced circulation of air (UFP 400, Memmert, Germany) at 80 °C for 4 h and dried at 40 °C for 12 h. Once the consolidation was completed, the samples were taken out of their molds.

The obtaining of porous cordierite-based materials was carried out by calcination (to burn out the starch) and reaction-sintering using an electric furnace with heater elements of SiC and employing the following thermal cycle: 1 °C/min up to 650 °C, 2 h; 3 °C/min up to 1330 °C, 4 h and cooling at 5 °C/min until room temperature.

The final materials were characterized by XRD (X'Pert PRO PANalytical) using radiation of  $\text{CuK}_\alpha$  at 40 kV and 40 mA, and open porosity measuring ( $P_o$ ) by the Archimedes method in water.

## 2.3. Mechanical evaluation of porous cordierite-based materials

Sintered bars were mechanically evaluated using 3-point bending from room temperature up to high temperature. The bars prepared with MCZ were tested at 1000 and 1100 °C, and those obtained from Premix were evaluated at 800 and 1000 °C. An INSTRON model 8501 servohydraulic machine with a cell of 100 kN maximum load and steel platen (HRc 65) and a silicon carbide (SiC) holder with span of 30 mm were used. The test were performed in displacement (of the actuator) control, with a constant rate of 0.1 mm/min which was previously adjusted in order to avoid temporal effects and to achieve an adequate arrangement of the sample in the load system. For high temperature testing, an electric furnace (SFL, UK) with heater elements of molybdenum disilicide ( $\text{MoSi}_2$ ) and a heating rate of 5 °C/min up to the test temperature were employed. Three to five bars of each set of compacts were mechanically tested.

From 3-point bending tests, load ( $F$ ) vs. deflection ( $y$ ) curves were obtained assuming that the stiffness of the assembly formed by the loading system and the SiC holder was high enough such that the displacement of the actuator matched the bar deflection. From these curves, the stress ( $\sigma$ ) vs. deflection ( $y$ ) relationship was determined by using the following equation (1):

$$\sigma = \frac{F \cdot L}{\pi \cdot R^3} \text{ [MPa]} \quad (1)$$

being  $F$  the applied load [kN],  $L$  the ‘span’ [mm] and  $R$  the bar radius [mm]. The mechanical strength of the bars ( $\sigma_F$ ) was considered as the maximum value of the stress in the  $\sigma$  vs.  $y$  curve. The Young’s modulus ( $E$ ) was calculated using the relation (2):

$$E = \frac{p \cdot L^3}{12 \cdot \pi \cdot R^4} \text{ [GPa]} \quad (2)$$

where  $p$  is the slope of the linear region of the  $F$  vs.  $y$  curve.

## 2. Results and discussion

Based on the XRD patterns corresponding to MCZ samples sintered at 1330 °C [Fig. 1(a)], cordierite (File N° 01-080-2316) as the main phase and mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ; File N° 01-074-2419) together with corundum ( $\alpha\text{-Al}_2\text{O}_3$ ; File N° 01-082-1399) as secondary phases, were identified. In contrast, for sintered Premix samples [Fig. 1(b)], exclusively cordierite was determined. It is worth noting that in XRD patterns of both samples and even more in the Premix sample, a low intensity band between 20 and 30° in  $2\theta$  was also identified. This band was assigned to the non-crystalline siliceous phases arising from impurities present in raw materials and reactions occurred among them to generate cordierite. The presence of a higher amount of glassy phase in bars prepared with Premix was also confirmed by the shiny appearance exhibited by surfaces of these samples. The formation of the glassy phase was studied in a previous work (Lambertini (2014)). It was proposed that the formation of this phase occurs by solid state reaction among mullite (coming from the kaolin decomposition), talc and silica (which comes from the decomposition of kaolin and talc), in the first place. Then, the formation of such liquid phase takes place by reaction of the unreacted protoenstatite (coming from talc), cordierite and silica grains, at a temperature lower than the eutectic point (1355 °C) due to the presence of impurities which form silicate-based phases with low melting points. Finally, these last phases react with mullite and/or alumina as temperature increases generating the growing of cordierite phase.

The bars obtained using MCZ and both starches presented higher open porosities ( $P_o$ ) than those prepared from Premix, as is shown in Table 1.

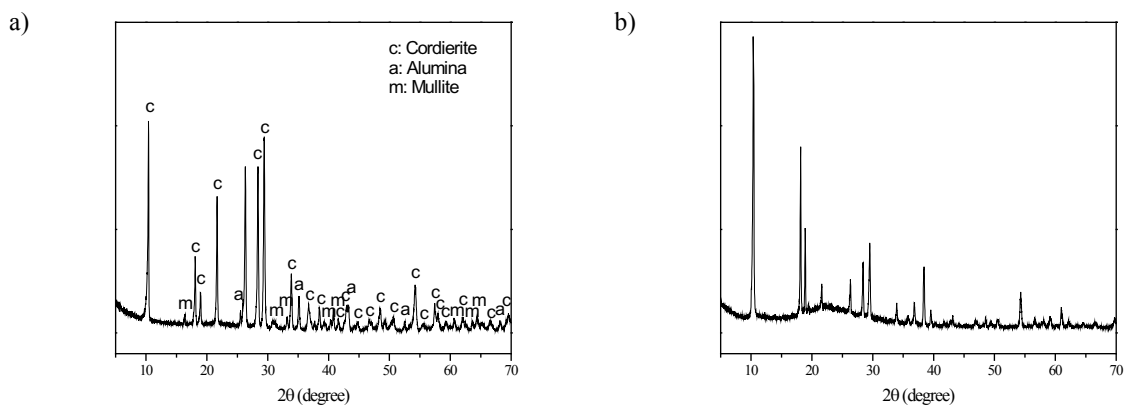


Fig. 1. XRD patterns of cordierite prepared from: (a) MCZ; (b) Premix.

Table 1. Open porosity and mechanical parameters of porous cordierite bars.

System	$P_o$ (%)	Testing temperature (°C)	$E$ (GPa)	$\sigma_F$ (MPa)
MCZ-potato	46±1	25	10±1	14±2
		1000	7±1	18±2
		1100	9±1	21±3
MCZ-corn	40±3	25	11±3	24±1
		1000	19±6	46±7
		1100	8±1	18±2
Premix-potato	21±1	25	29±7	58±4
		800	31±3	50±2
		1000	12±1	40±2
Premix-corn	2±2	25	53±5	97±13
		800	42±3	84±15
		1000	20±1	55±6

Typical stress vs. deflection curves for all of the systems are shown in Figs. 2 and 3. Bars prepared with Premix exhibited a linear behavior typical of a brittle and rigid material at room temperature as well as at 800 °C, in agreement with its low porosity and high content of glassy phase. However, the softening of the material was displayed at 1000 °C because the glassy phase which had a low viscosity at this temperature favored the sliding of grains promoting the viscous flow deformation.

The mechanical strength values obtained for Premix-corn system (Table 1) were similar to those reported for cordierite-based glass ceramics, supporting the role of the glassy phase (Mussler and Shafer (1984)). It was evident that the porosity of the specimens prepared with Premix did not play a relevant role in their mechanical behavior, although the lower values of the mechanical parameters  $\sigma_F$  and  $E$  of Premix-potato system could be associated with the higher porosity of these bars.

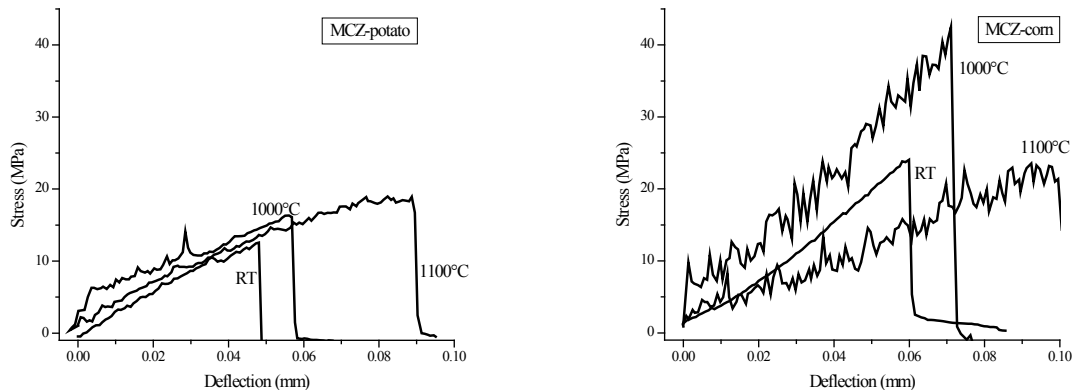


Fig. 2. Stress vs. deflection curves of MCZ-potato and MCZ-corn bars.

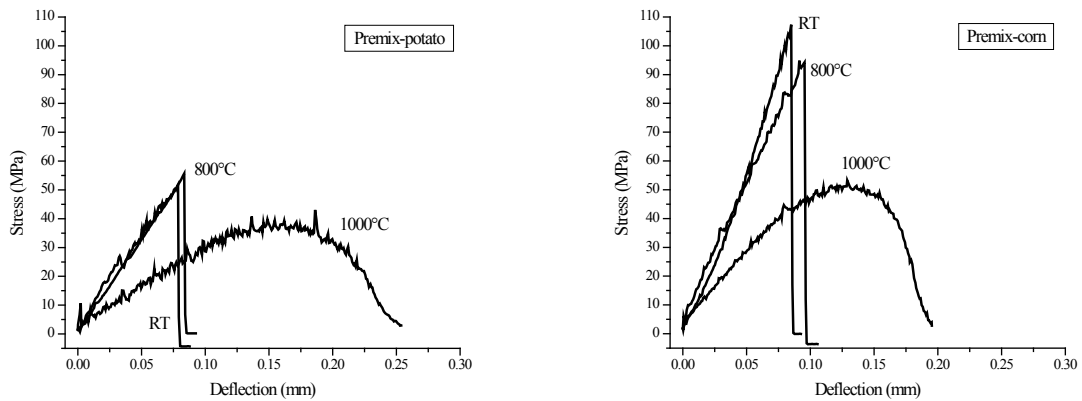


Fig. 3. Stress vs. deflection curves of Premix-potato and Premix-corn bars.

In the case of samples prepared with MCZ, the mechanical behavior was linear at room temperature and deviated from linearity for higher testing temperature although without softening. The smaller amount of glassy phase in the materials prepared with MCZ mixture in comparison with the Premix bars might justify these differences. However, the analysis of the parameters of MCZ specimens manifested that the porosity also played a role in the mechanical behavior, since the decrease expected considering the higher fluidity of the glassy phase was not observed in some cases. As can be observed in Table 1, the mechanical strength slightly increased as testing temperature increased for MCZ-potato bars while when corn starch was employed instead, this parameter only showed a significant increase between room temperature and 800 °C. The increase of the Young's modulus for bars prepared with MCZ and potato starch between room temperature and 800 °C and for those of the MCZ-corn system between 1000 and 1100 °C was remarkable.

The glassy phase softening as the testing temperature increased not only favored the viscous flow impoverishing the mechanical properties, but also could have a positive effect if it shielded the applied stress by crack tip blunting and stress relief by its own deformation. The final effect on the mechanical parameters will depend on the competence between both effects, i.e., if they mutually compensate or if one of them dominates the other one.

On the other hand, pores could occlude the viscous phase hindering its movement and reducing its negative effect. The occlusion is more significant as higher is the amount and smaller is the size of these pores. In the case of the used starches, it is known that the generated porosity is composed of large connected cavities, being the interconnections rather smaller ( $\sim 1\text{-}20\text{ }\mu\text{m}$ ). These connections are the main responsible for the restriction of the viscous phase movement (Sandoval et al. (2012)). In the cordierite material prepared using potato starch as consolidating agent, a higher porosity was generated when compared with that obtained when corn starch was used (Table 1). Moreover, previous studies using the same starches (Lambertini (2014)) determined that the cavities and interconnections when potato starch was used were somewhat larger than those generated when corn starch was employed.

From the compromise between the amount and the size of pores will result the occlusion degree of the viscous phase and the reduction of the viscous flow. Furthermore, this process will also compete with the stress shielding. The above-mentioned increase of the mechanical parameter at high temperature of bars prepared with MCZ was a result of this competition and manifested the role of the porosity in the mechanical behavior of these materials.

The dependence of  $\sigma_F$  and  $E$  parameters with porosity has been extensively studied and mathematical models relating them have been reported. Among the most used relationships are the following (equations (3) and (4)):

$$E = E^0 \cdot e^{-b\phi} \quad (3)$$

$$\sigma_F = \sigma_F^0 \cdot e^{-b'\phi} \quad (4)$$

where  $E^0$  and  $\sigma_F^0$  are the values of the properties for the solid without pores, and  $b$  and  $b'$  are used as fitting parameters. Considering the values of the mechanical parameters at room temperature for the materials prepared with MCZ where no effect of the viscous flow was present, and a value of 139 GPa as the Young's modulus and 245 MPa as the mechanical strength of cordierite without pores (Mussler and Shafer (1984)), the magnitude of  $b$  and  $b'$  were calculated using equations (3) and (4), respectively. A value  $\sim 6$  was obtained for both parameters, for the material prepared using potato starch as well as for that consolidated with corn starch. This magnitude was in the range of those values reported in the literature (Bailey and Hill (1970)): 3-5 for  $b$  and 3-11 for  $b'$ . This fact indicated that the porosity was determining of the mechanical parameters values of those bars prepared with MCZ (where no effect of the viscous phase was present).

### 3. Conclusion

Cordierite materials were prepared employing two precursor mixtures, MCZ and Premix, both based on kaolin, talc and alumina. Only the former mixture allowed the obtainment of a final porosity adequate for the use of these ceramics as thermal insulators. Moreover, the mechanical evaluation of the bars with less pores ( $< 20\%$ ) prepared with Premix that also contained the higher amount of glassy phase showed an impoverishment of the properties when testing temperature increased, especially at  $1000^\circ\text{C}$ . However, those specimens formed with MCZ and exhibiting the highest porosities ( $\geq 40\%$ ) showed a mechanical behavior mainly affected by the porosity, even increasing the values of the mechanical parameters when the testing temperature increased.

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